



Electron-impact ionization and photoionization of small organic solvents in the 15-200 eV range

Yen-Hsiang Huang, Grace H. Ho*, Zi-Xian Yang, Hung-M. Lin, Chang-Ying Chou, Chao-Chung Yang, Pei-Chen Lo

Department of Applied Chemistry, National University of Kaohsiung, Nanzih, Kaohsiung 811, Taiwan
*graceho@nuk.edu.tw

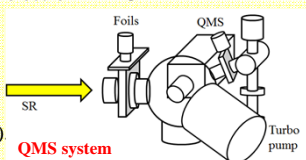
The PI and EI spectra of 12 organic solvents were examined in the threshold-200 eV range with a quadrupole mass spectrometer (QMS). The similarity or unlikeness of EI and PI pathways at the same impact energy will be presented: Solvents containing a carboxylate moiety will undergo mainly through the C(O)-OR bond breakage, whereas will have molecular ion as one of its major EI and PI products through the extensive threshold-200 eV range.

Introduction

The electron-impact ionization (EI) and photon-impact ionization (PI) of organic solvents in the ultraviolet and extreme ultraviolet (EUV) energy range are not only of fundamental interests, their underlying PI and EI chemistry are important for industrial applications, for example, in EUV lithography. We use 12 solvents as model molecules to demonstrate the capability of the outgassing facility at NSRRC in Taiwan to count gases in quality and quantity, making it one of limited facilities worldwide for evaluating EUV resists,. By examining the fragmentation patterns of the molecules after EI and PI in the threshold to 200 eV range, we try to make assessment about the choice of using EI or PI source for the resist testing.

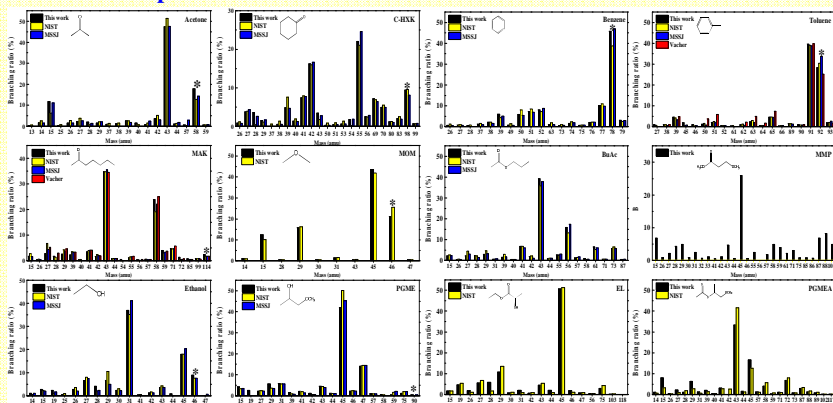
Experimental

- Light source:** 15 – 50 eV from BL04B1-Seya, and 50-200 eV from BL08A1-LSGM
- Electron source:** 15 – 150 eV from hot-emission electron in RGA
- Samples:** benzene, toluene (aromatics)
acetone, cyclohexanone, MAK (ketones)
dimethyl ether (ether); ethanol (alcohol);
PGME, BuAc, MMP, EL, PGMEA (oxycarbonyls)



Results and Summary

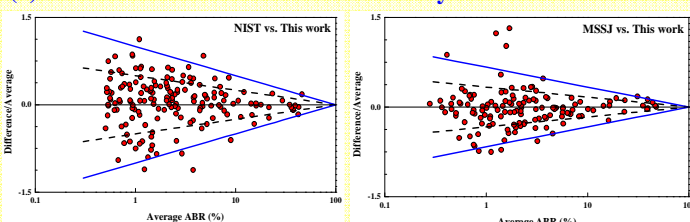
Electron impact ionization at 70 eV



- Our EI spectra consist with those reported by NIST[1], MSSJ[2] and Vacher [3,4].

How good is our EI and PI measurements?

(1) Instrument-to-instrument uncertainty

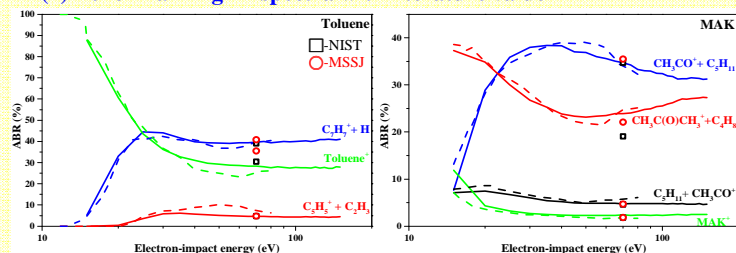


$$ABR_{m/z} = \frac{(I_{m/z}/T_{QMS,m/z})}{\sum_{m/z} (I_{m/z}/T_{QMS,m/z})}, \quad \text{Difference/average} = \frac{ABR_{m/z, \text{NIST or MSSJ}} - ABR_{m/z, \text{this work}}}{\frac{1}{2}(ABR_{m/z, \text{NIST or MSSJ}} + ABR_{m/z, \text{this work}})}$$

- Instrument-to-instrument (ItI) uncertainty: Differences in absolute branching ratios of ion production are mainly statistic.

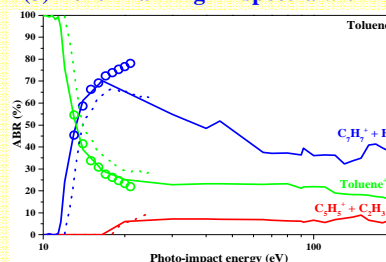
- The ItI uncertainty of this work wrt MSSJ (Hitachi series) is ~ 35% better than that wrt NIST.

(2) Benchmarking EI spectra with literature value



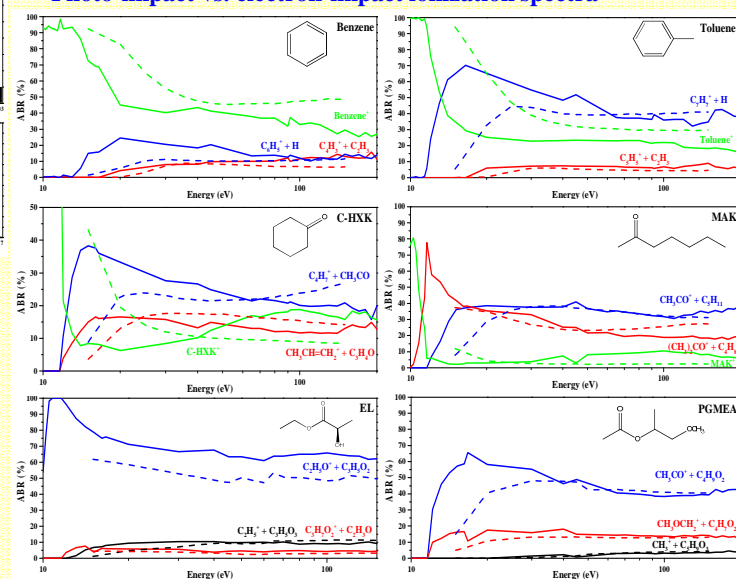
- Electron-impact ionization of this work (solid line) are consistent with Vacher's report (dash line) [3,4].

(3) Benchmarking EI spectra with literature value



- Photo-impact ionization of this work (solid line) is consistent with Taylor's (hollow dot) [5] in the 12-16 eV range. An energy offset is found in Shaw's report (dot line) [6].

Photo-impact vs. electron-impact ionization spectra



PI (solid line), EI (dash line)

- Molecular resistant against EUV:

→ Aromatics > ketones > ether and alcohols > esters

- Molecular integrity above 50 eV

→ Aromatics: EI > PI, Others (parent+ + direct fragmentation): PI > EI

[1] <http://webbook.nist.gov/chemistry/>

[2] Horai, H.; et al. *J. Mass. Spectrom.* **2010**, 45, 703-714

[3] Vacher, J. R.; Blin-Simiand, N.; Jorand, F.; Pasquiers, S. *Int. J. Mass spectrom.* **2005**, 240, 161-168.

[4] Vacher, J. R.; Jorand, F.; Blin-Simiand, N.; Pasquiers, S. *Chem. Phys. Lett.* **2007**, 434, 188-193.

[5] Stebbings, W. L.; Taylor, J. W. *Int. J. Mass Spectrom. Ion Phys.* **1972**, 9, 471-484.

[6] Shaw, D. A.; et al. *Chem. Phys.* **1998**, 230, 97-116.

Acknowledgement

National Science Council of Taiwan (NSC100-2120-M-009-010)